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THEORETICAL STUDIES OF [KMNO4]X USING FIRST PRINCIPLES CALCULATIONS

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Abstract:

In this study, using the Gaussian View program and using Stuttgart Dresden Triple Zeta (SDD) as the basis function, the detection of pure potassium permanganate dye KMnO4 doped with functional groups (x is 1NH2, 2NH2, 1CH3, 2CH3) were investigated. Electronic and spectral properties were examined. The electronic properties included the study of the HOMO and the LUMO gap, energy gap, electronic affinity, ionic potential, and the calculation of the energies in the ground state of the pure and doped dye. As for the spectral properties, it included the study of electronic transitions and the ratios of the transitions occurring in the energy levels by solving the time-dependent Schrödinger equation, as well as studying the infrared spectra to know the type of bonds and their locations.

Keywords: Potassium Permanganate, First Principles

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1. Introduction:

Potassium permanganate It is an inorganic compound with the chemical components KMnO4. It is a purple-black crystalline salt that dissolves in water as K + and MnO-4 to shape an excessive purple to red answer for wound cleaning and widely wide-spread disinfection. It's on the World Health Organization's listing of integral medicines [1] .In 2000, world manufacturing used to be estimated at 30,000 tons. Almost all functions of potassium permanganate advantage from its oxidative properties. [2] As a robust oxidant that does now not produce poisonous by-products, $KMnO_4$ has many area of interest purposes.

Potassium permanganate can be used to quantify whole oxidizable natural rely in water samples. The decided fee is known as the permanganate value. In analytical chemistry, in part aqueous $KMnO_4$ popular options are used as oxidative titrants (potassium permanganate) for redox titrations. When potassium permanganate is titrated, the answer turns mild purple, darkening as extra titrant is brought to the answer. Likewise, it is also used as a reagent for the determination of pulp kappa number. Oxalate reduction is commonly used to standardize $KMnO_4$ solutions.[3]

Potassium permanganate is produced industrially from manganese dioxide, which additionally happens in the shape of the mineral pyrolusite. In 2000, world manufacturing used to be estimated at 30,000 tonnes. [2] MnO_2 is melted with potassium hydroxide and heated in air or with different oxygen sources such as potassium nitrate or potassium chlorate. [2] This method produces potassium manganite :

$$2\ MnO_2 + 4\ KOH + O_2 \rightarrow 2\ K_2MnO_4 + 2\ H_2O$$

(In the case of sodium hydroxide, the last product is no longer sodium manganate however a manganese(V) compound, which is why potassium permanganate is greater often used than sodium permanganate. Also, potassium salts crystallize higher[3]. Potassium manganate is then converted to permanganate by electrolytic oxidation in an alkaline medium:

$$2\ K_2MnO_4 + 2\ H_2O \rightarrow 2\ KMnO_4 + 2\ KOH + H_2$$

Acidic aqueous answer of KMnO4 for series of gaseous mercury from flue fuel for the duration of stationary supply emission trying out[4]. In histology, potassium permanganate is old as a bleaching proxy.[5,6]

2. Computation method

The present work treats potassium permanganate with three parameters B3LYP (three-parameter exchange of Becke and Lee, Yang and Parr correlation functionals) (DFT) and SDD (Stuttgart-Dresden-Triple-Zeta-ECP (effective nuclear potential)) . electronic structure. place. Calculate electronic properties using Koopman's theorem. Perform excitation energy and vibrational transitions using time-dependent TD density functional theory.

3. Results and discussion

3.1. The Structure of Molecular

The structures of pure potassium permanganate and doped potassium permanganate were designed using Gauss View 5.0.8 and using the Gaussian 09 package using DFT with B3LYP/SDD levels. Figure 1 shows the optimized relaxed structures of pure and doped potassium permanganate.

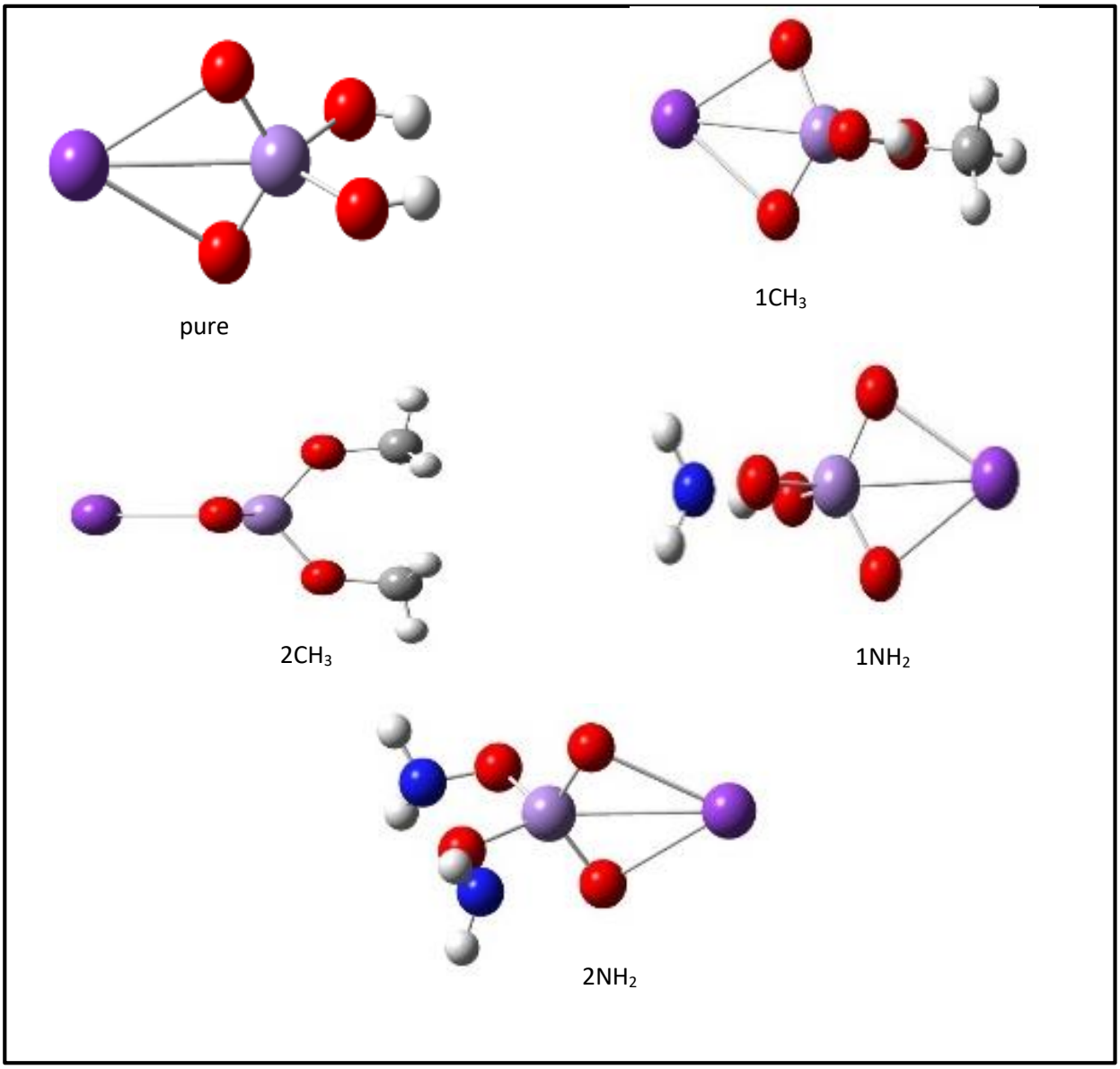


Fig. 1: The relax structure of the pure and doped potassium permanganate. by DFT-B3LYP/SDD.

3.2 electronic properties

Table 1 The calculated values of excessive occupied molecular orbital power E_{HOMO}, low molecular orbital strength E_{LUMO} and power hole E_{gap} in eV for pure potassium permanganate and doped potassium permanganate are proven. As shown in Figure 2, E_{LUMO} is larger than E_{HOMO}. This end result is in correct settlement with the bring about ref. [7] and pointed out that potassium permanganate requires high energy to donate or accept electrons, and potassium permanganate has insulating behavior. The LUMOs are greater than the HOMOs and they are distributed according to a linear combination of atomic orbitals.

Table 1: The E_{HOMO}, E_{LUMO} and E_{gap} in eV of pure and doped potassium permanganate

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	Egap (eV)
Pure	-5.7812	-2.3420	3.4392
1NH2	-5.3812	-2.0778	3.3034
1CH3	-5.4983	-2.1886	3.3097
2NH2	-5.1641	-2.0631	3.1010
2CH3	-5.2006	-2.0661	3.1344

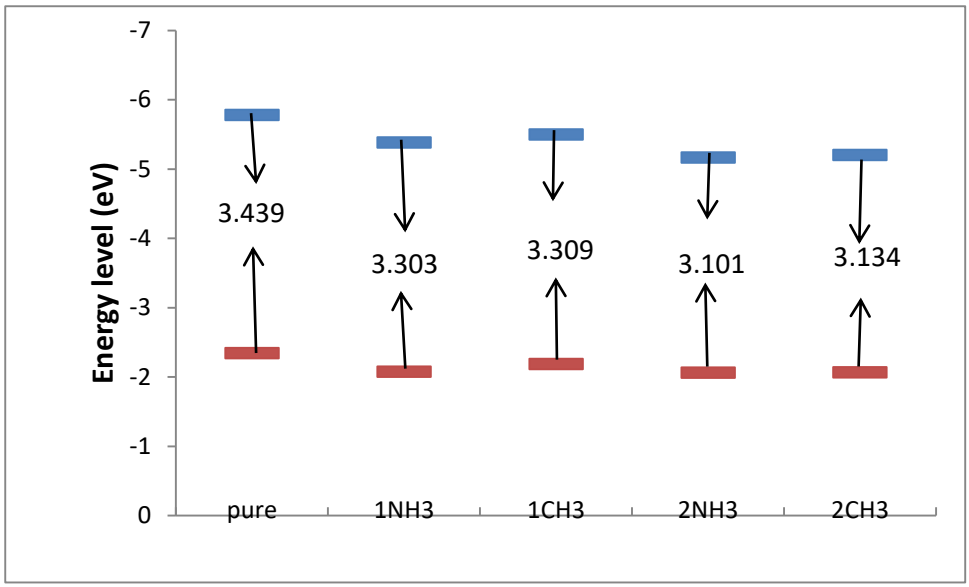


Fig. 2: The E_{LUMO} and E_{HOMO} of pure and doped potassium permanganate from B3LYP/SDD level.

Table 2 illustrates the calculated values of some electronic variables for pure and doped potassium permanganate from the B3LYP/SDD density functional theory. The total ground state energy E_T of a compound is approximately the sum of the E_T of all atoms in the compound.

The results showed the virial ratio (-V/ T) for pure and doped potassium permanganate lies in the same range for such systems, this an indication to a suitable basis set used for the relaxation of the studied complex.

The ionization energy I_E and electron affinity E_A of pure potassium permanganate and doped potassium permanganate were calculated according to Koopmans theorem, these values indicate that pure potassium permanganate and doped potassium permanganate require higher energy to provide/ Accepting electrons to form cations/anions can be low at I_E and E_A. On the other hand, the calculated values of electronegativity EN and electrochemical hardness H show that pure and doped potassium permanganate have lower electron transfer ability. High H refers to the high excitation energy required for electron transfer, pure and doped potassium permanganate is an electrochemically hard compound

The calculated electronic softness value S reflects the large gap between the valence and conduction bands, the large gap between pure potassium permanganate and doped potassium permanganate, and the low softness.

Table 2: The results of some electronic properties of pure and doped potassium permanganate.

Electronic Properties	E_T (a. u)	I_E (eV)	E_A (eV)	E_N (eV)	H (eV)	S $(eV)^{-1}$	-V/T
Pure	-434.871	5.781	2.3420	4.0616	1.7196	0.2908	2.0057
1NH2	-490.174	5.381	2.0778	3.7295	1.6517	0.3027	2.0297
1CH3	-474.166	5.498	2.1886	3.8434	1.6548	0.3021	2.0278
2NH2	-545.463	5.164	2.0631	3.6136	1.5505	0.3225	2.029
2CH3	-513.453	5.200	2.0661	3.6333	1.5672	0.3190	2.028

3.3 spectral properties

From the comfortable molecular systems determined the usage of the B3LYP/SDD-DFT technique, the UV-Vis spectra of the UV and seen areas of the studied compounds had been tested and analyzed the usage of a time-established self-steady discipline TD-SCF technique with the identical blending feature and foundation set. A key issue for the software of compounds as photovoltaic substances is the absorption spectrum of the compound, which corresponds to the sun spectrum.

Figure 3 illustrates that the pure potassium permanganate has two direct transitions from the valence band to conduction band with absorption wave lengths 645.78 and 620.10) nm. The doped potassium permanganate with $1NH_2$ has direct transitions from the valence to conduction with absorption wave lengths 1632.0039, 688.490, and 570.01) nm. The doped potassium permanganate with $2NH_2$ has also direct transition HOMO→LUMO with wave length 1403.796 ,626.970 and 1970.804nm. The other doped potassium permanganate have indirect transitions. Table 3 The calculated values of absorption energy E_{abs} (eV), absorption wavelength λ_{max} (nm), oscillator strength O.S, molecular orbital characteristic MOC%, and transition state are described.

Table 1: Excitation energy, oscillator strength and transition states HOMO→LUMO .

Compounds	Excitation Energy $(cm)^{-1}$	Wave Length (nm)	Oscillator Strength	Transitions HOMO→LUMO
Pure	15485.14	645.78	0.0003	HOMO-> L+1 (33%) HOMO->L+2 (64%)
	16126.36	620.10	0.0008	HOMO -> L+4 (95%) HOMO-7->L+4 (3%)
$1NH_2$	6127.43	1632.00	0.0	HOMO->LUMO (91%) H-1->LUMO (9%)
	14524.53	688.49	0.0001	HOMO->L+1 (22%), HOMO->L+2 (58%) H-1->L+2 (6%) HOMO->L+4 (8%)

	17543.48	570.01	0.001	HOMO->L+4 (74%) H-7->L+4 (3%) H-1->L+4 (9%) HOMO->L+1 (5%) HOMO->L+2 (5%)
2NH2	7123.53	1403.796	0.0002	H-1->LUMO (59%) HOMO->LUMO (37%) H-7->LUMO (2%) H-4->LUMO (3%)
	15949.724	626.97	0.0	H-1->LUMO (35%), HOMO->LUMO (59%) H-1->L+4 (2%) HOMO->L+4 (2%)
	5074.06	1970.80	0.0001	H-1->LUMO (57%), HOMO->LUMO (42%) H-7->LUMO (2%) H-3->LUMO (3%)
1CH3	1659.09	6027.38	0.0	H-2->LUMO (10%) HOMO>LUMO(132%)
	9869.06	1013.26	0.0002	HOMO->L+1 (88%) H-2->L+1 (5%) HOMO->L+3 (2%)
	13127.57	761.75	0.0006	HOMO->L+4 (72%) H-2->L+4 (7%) HOMO->L+2 (9%) HOMO->L+3 (3%)
2CH3	4539.31	2202.97	0.0	HOMO->LUMO (100%)

	13705.87	729.61	0.0009	HOMO->L+4 (92%) H-7->L+4 (3%)
	10547.38	948.10	0.0007	HOMO->L+1 (44%) HOMO->L+2 (56%)

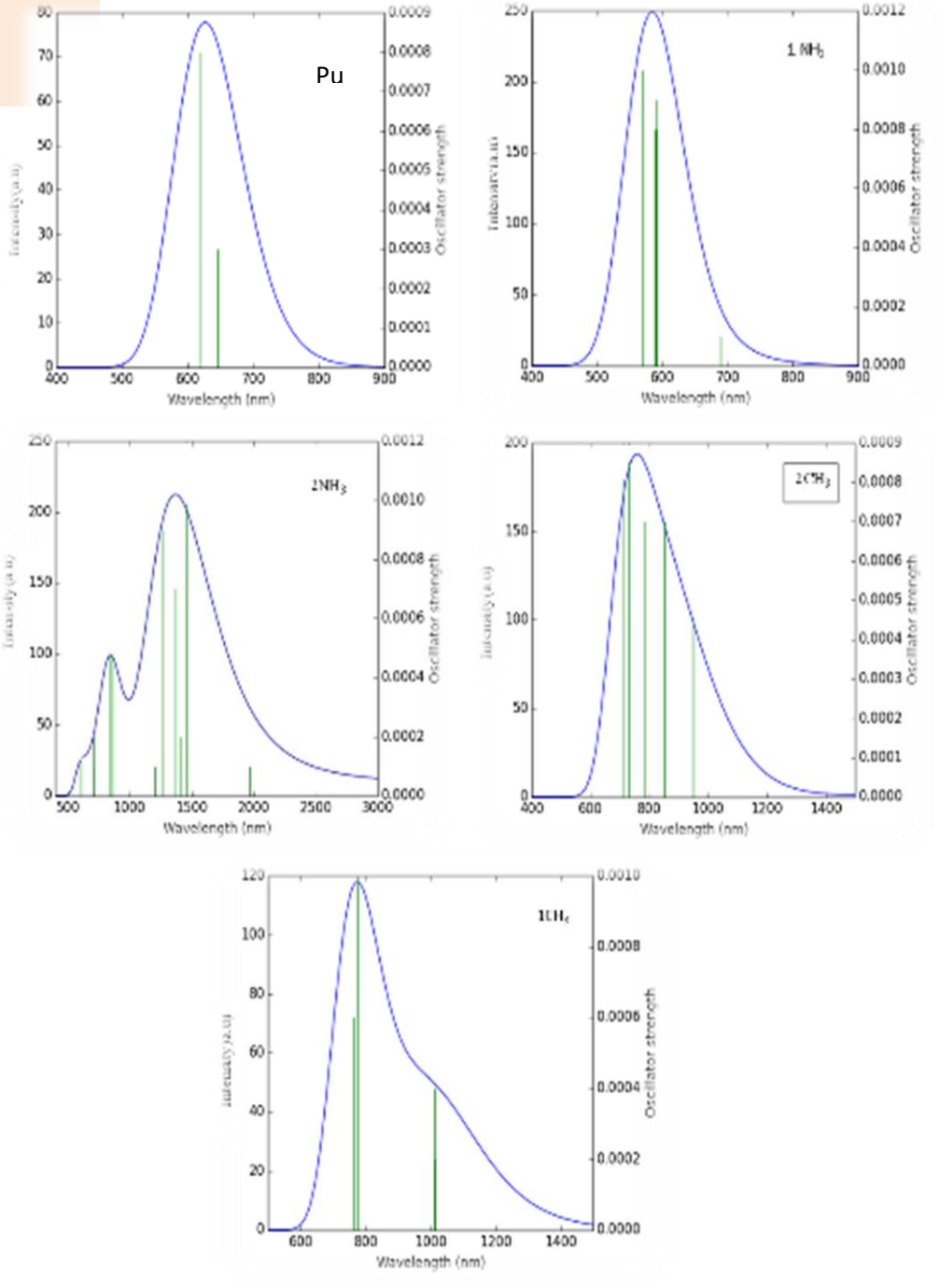


Figure 3: UV-Vis Spectra of the compounds.

Infrared spectroscopy exploits the truth that molecules take in frequencies function in their structure. These absorptions arise on the resonant frequency H. The frequency of the absorbed radiation coincides with the vibration frequency. The electricity is suffering from the form of the molecular capacity electricity surface, the mass of the atoms, and the vibrational coupling involved. For an "infrared active" vibrational mode with inside the sample, it have to be followed through a extrade with inside the dipole second. Permanent dipoles aren't required, as generally handiest the dipole second desires to be changed[8]

Molecules can vibrate in lots of ways, every of that's known as a vibrational mode. For a molecule with N atoms, geometrically linear molecules have 3N-five vibrational modes, whilst nonlinear molecules have 3N-6 vibrational modes (additionally called vibrational ranges of freedom).

The infrared IR spectra of pure and doped potassium permanganate molecules group are provided in figure (4).

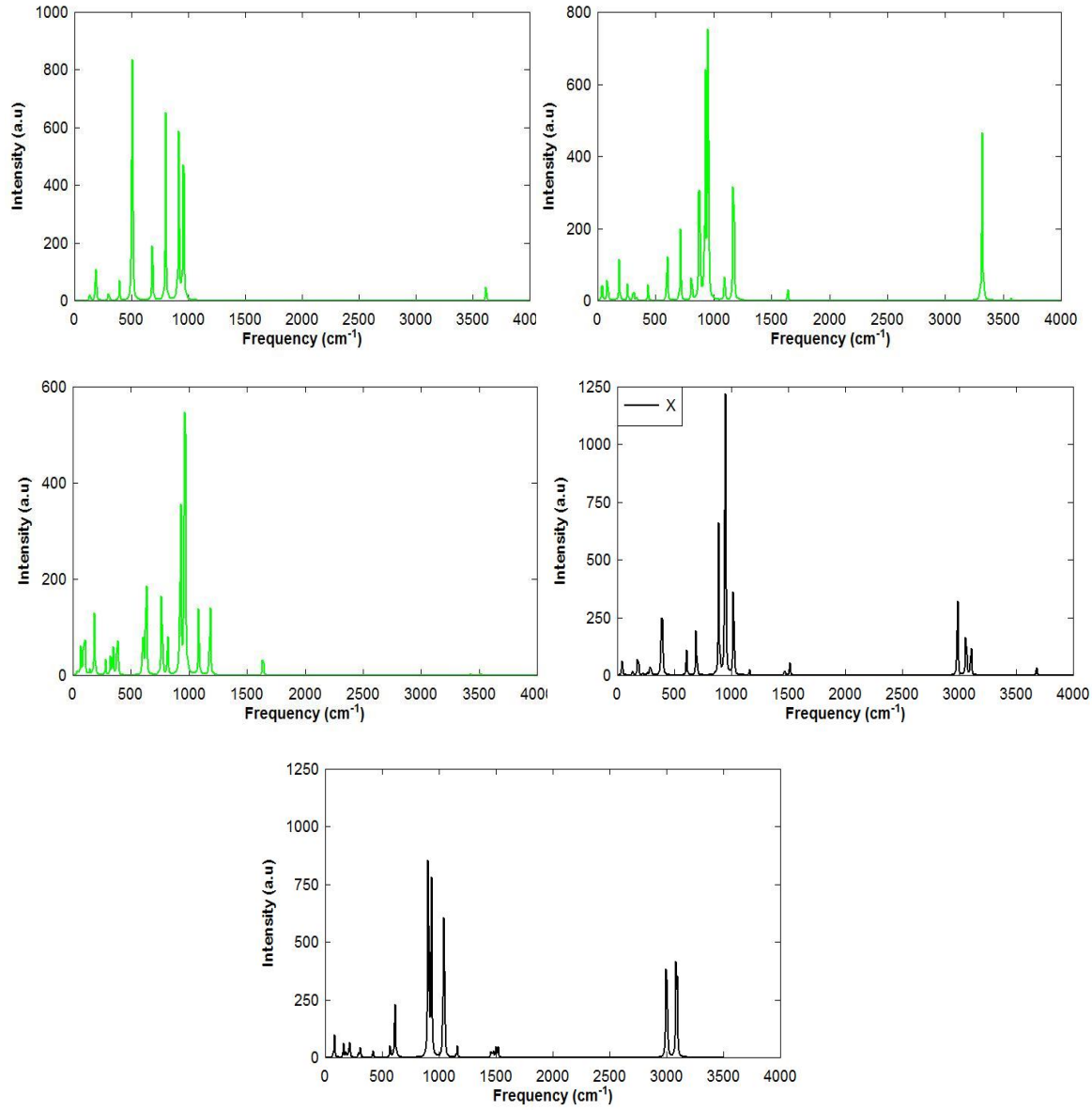
Vibrational spectrum was calculated for the system and has been split into two regions, a low wave number fingerprint region ($< 300\text{cm}^{-1}$) is the first region, and the second is a high wave number region $(1600 - 4000)\ \text{cm}^{-1}$.

The aromatic molecular chain in the (2900-3250)cm^(-1) region, which is a distinguishing region that facilitates the identification of the (C-H) chain, including two regions, the (3100-3250)cm^(-1) region is used for asymmetric stretching and (2900-3100)cm^(-1) for symmetric stretching mode [9]. The total number of vibrations of normal modes can be calculated by 3N-6 and it equals to 18-24-30-27-36 modes of the pure ,$1NH_2$,$2NH_2$,$1CH_3$and $2CH_3$ respectively

. The observed value of (C-H) stretching vibrations of the studied compounds molecular system in the region is $(3085.94 - 3196.85)\text{cm}^{-1}$. In this system the absorption in the region 3000cm^{-1} refers that hydrogens are append to sp^2 carbon ($> 3000\text{cm}^{-1}$) but not to carbons sp^3 ($< 3000\text{cm}^{-1}$) [9]. The frequencies of aromatic molecules have both in-plane $(1100 - 1700)cm^{-1}$ and out-of-plane ($< 1000\text{cm}^{-1}$) bending vibrations. A molecular system in this study, the in-plane vibrations are calculated at $(1112.64 - 1643.94)\text{cm}^{-1}$ from DFT/B3LYP with SDD basis sets, and the out-of-plane (C-H) bending vibrations are observed in the region $(836.07 - 929.69)\text{cm}^{-1}$.

The (C-C) stretching for molecular system is observed at $(1597.34 - 1643.94)\text{cm}^{-1}$. From B3LYP/ SDD calculations, the $C - NH_2$ stretching occurs at $1650.06\ \text{cm}^{-1}$and the (H-C-O) stretching occurs at $1752.23\ \text{cm}^{-1}$.

In aromatic compounds NH_2, the (N-H) stretching frequencies in the region $(3300 - 3700)\text{cm}^{-1}$, the (N-H) symmetric stretching modes located at $(3521.52 - 3619.88)\text{cm}^{-1}$ and the asymmetric stretching modes appear at 3650.60 from DFT calculation. Moreover, the NH_2 group shows rocking, scissoring, wagging and torsion modes, The stretching (H-C-O) bond experimentally observed at 1750cm^{-1}[10,11], from B3LYP calculated the value appear at$(1752.23,1768.44)\text{cm}^{-1}$.



4. Conclusions

1- By observing the virial ratio, we concluded that the SDD basis set were very suitable for this type of molecules.

2- Pure and doped potassium permanganate have an energy gap located within the semiconductor and this makes it of different electronic applications.

3- Through electronic transmissions, we concluded that there are direct and indirect electronic transmissions.

4- In the case of high frequencies, we notice the occurrence of stretching absorption in the case of high frequencies, bending absorption is occurred.

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